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Materials surface science applied to the investigation of cultural heritage artefacts

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Abstract

The skill of ancient artisans manufacturing artistic or everyday artworks surprises the modern material scientists. We show, through the study of archaeological pieces, how laboratory research instruments use enlightens the fabrication processes of unique items at antic periods. The specificity of surface science research favouring non-invasive means for investigations on museum objects is emphasised. The examples concern:

- Nanostructured layers on ceramic surface to obtain the so-called *lustre* effect, invented by ancient Islam potters;
- Intentional coloration of metallic objects by chemical patination, attested in Egypt on 2nd millenary BC and still applied by Japanese artisans;
- The history of gilding objects: leaf gilding, mercury gilding, and other processes;
- The Fresco technique, a perennial wall painting, known by ancient Roman and propagated through centuries.

The examples open new fields belonging to the modern materials science, to understand the mechanism involved in processes with the constraint that one does not know all the fabrication steps.

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Keywords: Cultural heritage; Surface science; Ion beam analyses; Lustered ceramic; Metal patination; Metal gilding; Fresco

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1. Introduction

The scientific investigation on cultural heritage items in materials laboratory has suffered very important developments during the last decades, due to the growing interest of the general public together with the demand of collection and museum keeper for a better understanding of the archaeological, artistic and technical history of those items.

Meanwhile the quality and performance of the research equipment available in these materials laboratories has been drastically improved, leading to the possibility to obtain more and more information on the objects. However the investigation on unique artistic or archaeological objects is subject to specific constraints to be kept in mind:

- The first is to favour as much as possible, especially for museum items, the non-destructive or non-intrusive measurement means;
- The second is to gather as much as possible existing information about the item history: date of production, period and conditions of use or exhibition, eventual abandonment and conditions of conservation, preservation in collection or museum, possible ancient or modern intervention of repair or restoration, etc.
- The third is to conclude a collaboration agreement with the item “keeper”, archaeologist, museum curator, collection owner, about the aims and the limits of the undertaken laboratory investigation: is it for documentation only or for preparing a restoration or as a part of a general research program?, has it to be fully non-invasive?, is microsampling allowed?, etc.

The consequence of those constraints is that the dominating scientific domain to be applied to cultural heritage objects laboratory investigation is *surface science*. That scientific domain underwent quite recently very spectacular developments in its application to patrimonial items (Aucouturier and Ceretti 2007). In particular the performances of available research instruments used in the devoted laboratories underwent impressing improvements, especially in the field of the non-invasive measurements: X-ray fluorescence (XRF), X-ray diffraction (XRD), Raman or infrared micro-spectrometry, ion beam analyses (IBA), etc. (Janssens and Van Grieken 2004).

The present paper will try to illustrate the results and the limits of that specific approach, through examples taken from several research programs conducted on more or less ancient objects. We shall not consider the material of easel paintings and focus the examples only on three dimensional objects constituted of various materials: ceramic, metal, gilded metal and wall fresco.

ere introduce the paper, and put a nomenclature if necessary, in a box with the same font size as the rest of the paper. The paragraphs continue from here and are only separated by headings, subheadings, images and formulae. The section headings are arranged by numbers, bold and 10 pt. Here follows further instructions for authors.

2. Glazed ceramics with metallic lustre

In the 9th century, during the most brilliant period of Islamic civilisation in Mesopotamia, under the Abbasid caliphate, appeared an outstanding technique of ceramic decoration: lustre, a precursory nanotechnology, a true alchemy which is able to transform simple earth into infinitely precious objects, giving them magnificent shine, including the appearance of gold (Caiger-Smith 1985). That kind of decoration is related to a very sophisticated process which creates on the surface of a glazed ceramic a layer of vitreous matter with sub-micron thickness containing metallic particles (copper and silver) with a nanometric diameter (Kingery and Vandiver 2004, Perez-Aranteguy et al. 2001). It confers upon the surface a particular coloured aspect, often metallic in specular reflection but still shining in different directions.

The fabrication and use of lusted ceramics were propagated across the Islamic world (Egypt, Syria, Iran, Maghreb countries) as far as Spain, leading to the creation of the Italian lusted majolica in the Renaissance period (fig. 1).

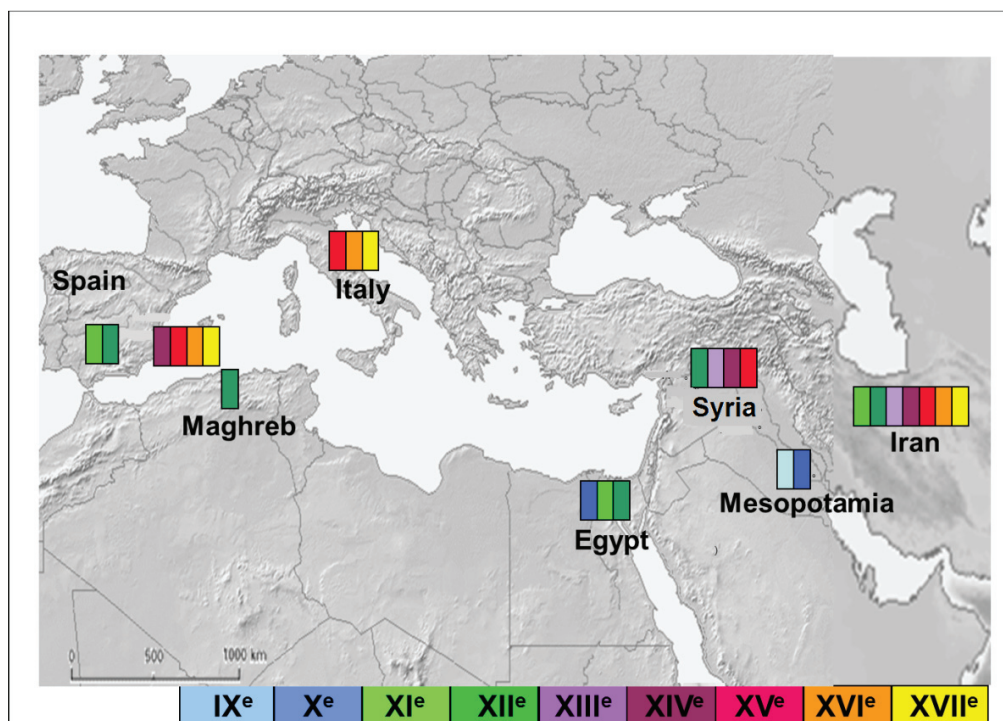


Fig. 1: The routes of the lustre. Origin and dating of the studied objects

The lustred ceramics are obtained by a specific process including three steps of firing summarized in fig.2, successively paste, glaze and lustre firings; the last one is done under reductive atmosphere.

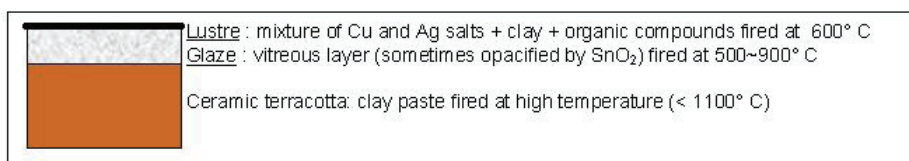


Fig. 2: Schematic process of lustred ceramic elaboration

A collaboration was established with three French national museums (Louvre museum, Musée national du Moyen Age and Musée national de Céramique de Sèvres), an Italian museum (Gubbio town museum) and a private collector. More than hundred objects (shards, plates, *Albarell*o, etc.) could be studied and fully described (Chabanne et al. 2012, Padeletti et al. 2010, Politi et al. 2014). Fig. 3 shows some examples of the studied items.



Figure 3: Examples of lusted objects (whole pieces or fragments): Abbasid period (A & B, Louvre museum), Fatimid period (C & D, Louvre museum) and Hispano-Moresque period (E & F, museum of Middle age, Paris)

2.1. Experimental

The best adapted method for that study is IBA: particle-induced X-ray emission (PIXE) under a proton beam gives the elemental composition of the first surface layers and Rutherford backscattering spectrometry (RBS) leads to a possible profiling of the elemental composition from the surface (Calligaro et al. 2004). Some microsampling was allowed on the shards to precise the glaze composition by microanalysis in the scanning electron microscope (SEM-EDS).

For IBA, we use the particle accelerator AGLAE which delivers beams of proton or alpha particles of a few MeV (3 MeV here). The beam is extracted to the open atmosphere, allowing a direct analysis of the object whatever its size. PIXE under 3 MeV protons gives the average elemental composition of the glaze over the first 20-40 μm from the surface with an accuracy better than 10 relative %. When sampling was possible the composition was confirmed by SEM-EDS of those samples.

RBS under 3 MeV alpha particles allows a quantitative profiling of the same elements over the first micrometres from the surface. A simulation code (SIMNRA (Mayer 1997-98)) is used to interpret the RBS spectra; it describes the analysed depth as a series of layers of adjustable compositions and thicknesses. In a few number of cases, the result is confirmed by transmission electron microscopy on a thinned cross-section (Fig. 4). That simulation leads to an evaluation of the quantity of metal (silver and/or copper) nanoparticles, their position as respect to the surface and the thickness of the different layers.

In complement, XRD with a grazing incidence (less than 5 degrees) have been performed only on shards (for space availability) to measure the broadening of the copper and silver diffraction peaks due to the nanometre size of the metal nanoparticles. That broadening is used to evaluate the diameter of the nanoparticles (Guinier 1964).

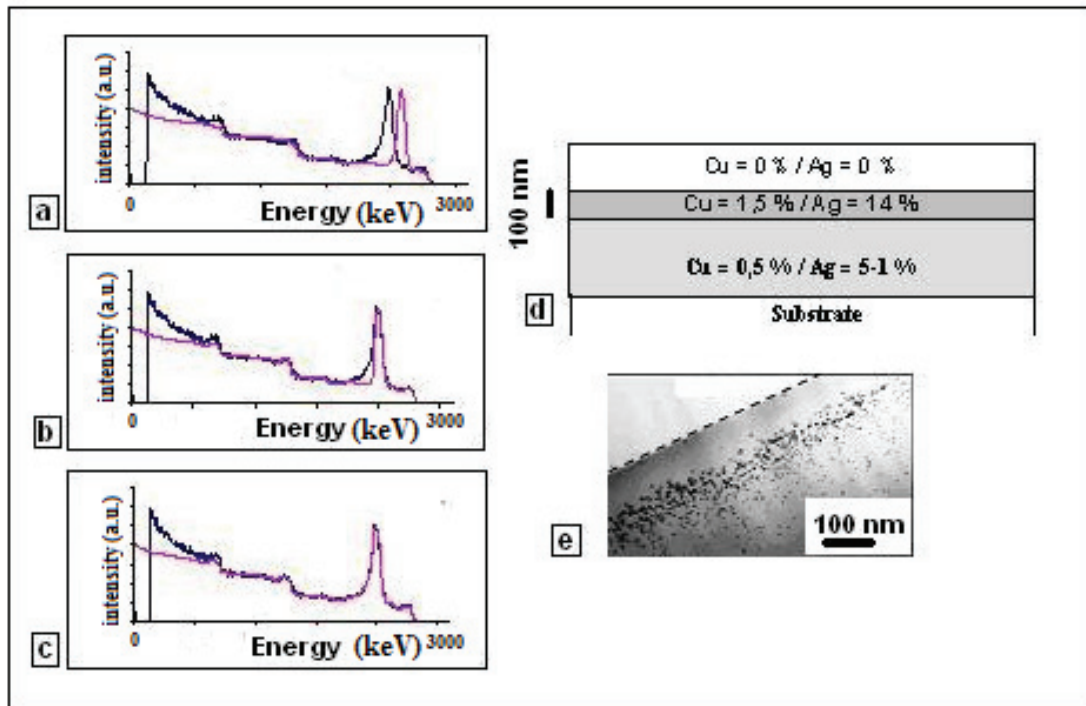


Fig. 4: Experimental (curves with noise) and simulated RBS spectra on a specimen of lustrous ceramic; (a) simulation of the glaze covered with a layer containing Cu and Ag; (b) addition of a layer containing neither copper nor silver; (c) insertion of an intermediary layer with a Cu and/or Ag gradient; (d) simplified result of the simulation; (e) TEM image of a cross section of a similar specimen (© CEMES, P. Sciau).

2.2. Results

It is not possible to give here the detailed results of the full program. Those may be found in the cited publications (Chabanne et al. 2012, Padeletti et al. 2010, Politi et al. 2014) or the references therein included. Fig. 5 shows three examples of the obtained values for lustrous ceramics with two different origins. As visible from that figure and confirmed during the whole program, the microstructure of the surface lustre layers may be very different from a production to another. The thickness of the layer containing the metal nanoparticles varies from more than 1 μm to a few hundred nanometers. It may be less than 100 nm for the Italian majolica. That layer may be covered with a glassy nanometric layer which contains no metal at all. That microstructure contributes evidently definitely to the visual aspect of the lustrous ceramic.

The general conclusions of the study are the following:

- Only the Abbassid (IXth cent.) and the Italian (Renaissance XVIth cent.) potters were able to obtain on the same object a polychrome lustre. The other lustre are all monochrome, from red to yellow but on different objects;
- During the propagation of the technique in the Islamic world, most potters used to adapt their “lustering” process to their ancient ceramic elaboration technique, instead of changing the ceramic elaboration process to prepare the following lustre application. It seems to not be the case for the Hispano-Moresque potters at the end of the XVIth century;
- Italian potters of the Renaissance period reached around the year 1520 the best technical skill for lustre decoration. Some of the analysed “historiato” plates (plates with a paint of an historical scenery) show lustrous details with a lateral acuteness better than 1 or 2 mm.

In complement XRD measurements were done directly on the surface of Mesopotamian, Egyptian and Spanish Hispano-Moresque lustrous shards to obtain an estimation of the metal particle diameters. Those diameters vary in

large proportion: between 10 and 20 nanometers in the first Abbassid production, they may reach more than 50 nanometers in the Renaissance Spanish shards. This shows that the lustre firing conditions have been very different from one site to the other.

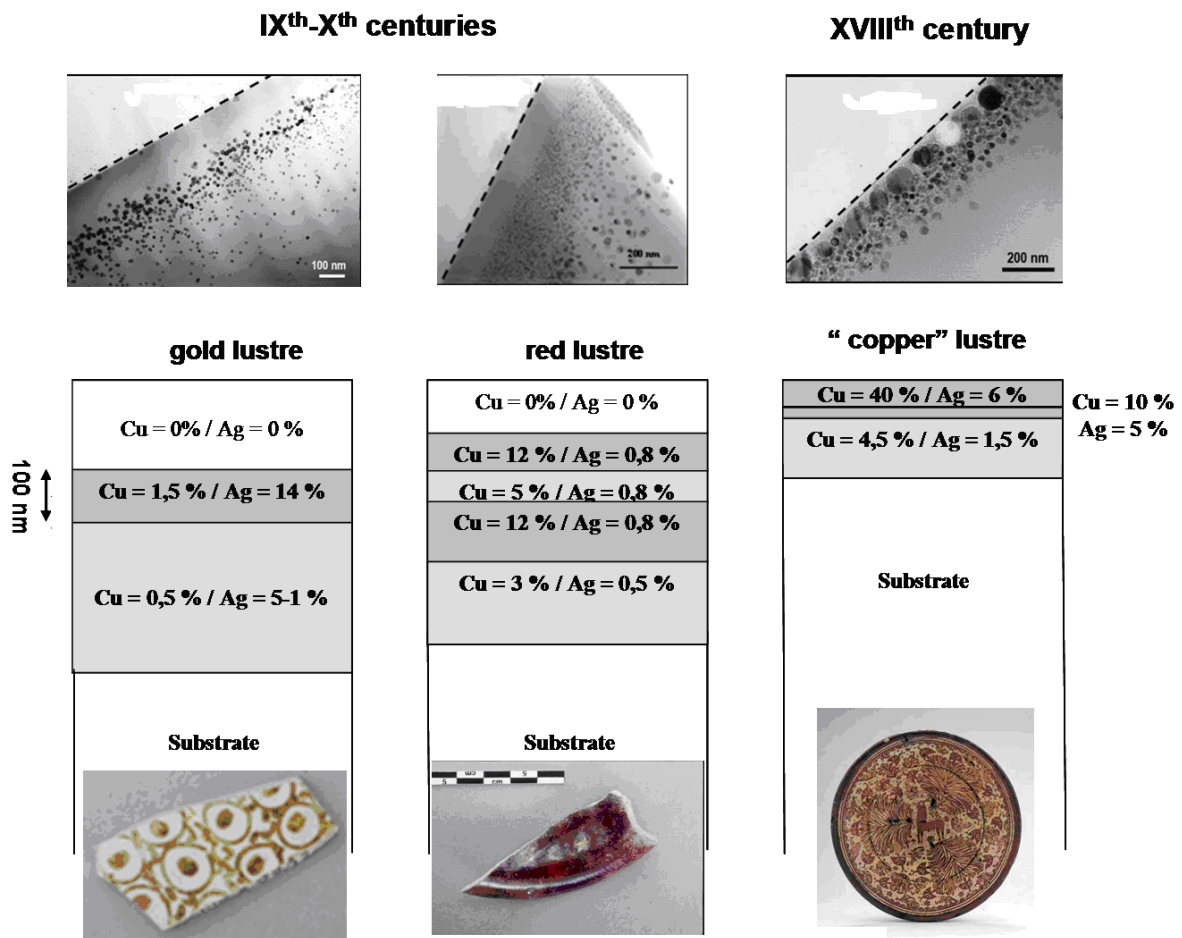


Fig. 5: Three lustre structures observed in TEM and corresponding results by RBS analysis simulation. TEM micrographs kindly provided by P. Sciau; concentrations in at. %.

3. Antic metal intentional patination Glazed ceramics with metallic lustre

Polychromy has been used by metal craftsmen from far antiquity. One may suppose that, as soon as metal alloying appeared, it was used to vary the colour of created objects. As far as copper-based alloys are concerned, it is now clear that metal artefacts fabricated in Mesopotamia as early as the third millennium BC, or in Egypt during the second millennium BC, were intentionally made of various alloys assembled or juxtaposed in order to show a combination of colour, improving the artistic effect.

Another process for controlling the colour of metal objects or parts of them is to submit the surface to intentional chemical treatments. Chemical treatments were very soon invented to build on the alloy surface a compound (generally oxidised) layer, with a given colour. This is usually called intentional patination. It is now known that this process appeared quite early for colouring bronze items with a dark layer, at least in Egypt at the beginning of the second millennium BC (Craddock and Giumlia-Mair 1993). The generic term used for that kind of patinated alloy is

black bronze or black copper. What is interesting about that kind of treatment is that the recipe propagated successively (or was re-invented?) to the Aegean bronze workers on the middle of the second millennium BC to decorate the swords found in Mycenae and dated from about 1500 years BC, then probably to the antic Greek artisans, and further also to the Roman bronze workers, with the name of Corinthian bronze. It is even used in the modern time in Japan from the XIVth century for decorative objects or sword hilts, and the alloy is there named Shakudo.

The characteristic of black bronze is that it is obtained by chemical action on the surface of bronze (Cu-Sn-Pb alloy) or copper, but that metal was intentionally alloyed with small additions of gold (0.2 to 8 wt % Au) and/or silver (0.2 to some percent Ag). The chemical recipe is known for the Japanese Shakudo (Murakami 1993), but not for the antic black bronzes. The result is the formation of a black surface layer of cuprous oxide Cu_2O . It is well-known that Cu_2O , commonly called cuprite, is of red colour. The fact that the surface oxide layer is black was not fully understood (Murakami 1993) until recent studies which will be discussed below. Figures 6 and 7 show some examples of black bronzes belonging to objects from the Louvre museum, which were studied in the C2RMF laboratory (Mathis 2005, Mathis et al. 2007).

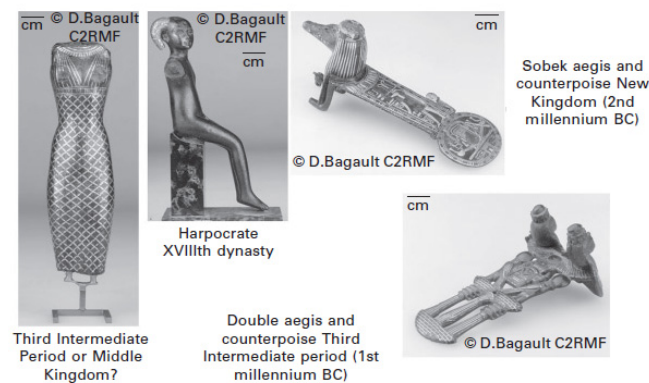


Fig. 6: Egyptian black bronze objects (with Au or Ag inlays) (1st and 2nd millenary BC) from the Louvre museum (DAE)



Fig. 7: Roman Bronze objects (1st and 4th century AD) inlaid with black bronze (and other metals).

3.1 Experimental

As the studied object decorated with black patina were all unique museum objects the study had to be as much as possible entirely with non-destructive methods, except very small chips sampling (by microdrilling) to identify the base alloys. The particle accelerator AGLAE was used, only with a beam of 3 MeV protons because the patinas were too thick (more than a few μm) for an alpha particle beam. The measurements were exploited in both PIXE and RBS modes as discussed above. It was not possible to obtain the exact elemental bulk analysis of the patinated inlays of the Roman objects, as the PIXE measurements integrate the composition of that patina and the bulk metal together, and metal sampling is evidently not possible.

XRD was also performed with a grazing incidence (less than 5 degrees) to identify the nature and the structure of the patina. It was completed with micro-Raman analyses.

With the help of a friend laboratory (EMat, University of Antwerp, Belgium), it was possible to obtain TEM cross section examinations on laboratory reconstruction of black bronze, using a Japanese recipe (unpublished results).

3.2 Results and interpretation

From the IBA analyses, it appears that the patinated alloys as well as their patina contain always gold and/or silver. The bulk concentration in Gold or silver of the Egyptian items is of 1 to 3 wt %. The inlays of the Roman objects contain also gold and silver

The intentional black patina has always the composition of cuprite Cu_2O and is enriched in precious metal. Some other elements, as sulphur and exceeding oxygen may bring information about the recipe used by the ancient artisans (presence of copper sulphate or sulphite in the oxidising solution?), but it is presently not possible to give more details about that recipe. The thickness of the oxide layer, measured by RBS, is quite large, often larger than 20 μm , the maximum attainable by RBS from the surface in the operating conditions. It is to compare with the known thickness of Japanese black patina on Shakudo, which is generally less than 2 or 3 μm (Murakami 1993). XRD and micro-Raman analyses confirm that the patina has the structure of cuprite.

A more interesting and important result was obtained with XRD: the patterns show the existence of metallic gold or silver inside the patina layer (it is not possible to distinguish between Au and Ag which have very close network parameters).

That result is very informative to understand why cuprite becomes black on black bronzes. During the oxidation process to elaborate the patina from a liquid solution, the electrochemical conditions are such that only copper is moderately oxidized (Cu_2O is produced instead of the cupric oxide CuO). Gold and silver contained in the alloy are not oxidized and remain in the patina in their metallic state, because the temperature is too low to make them diffuse downward into the non-oxidized substrate. Those metals precipitate as nanoparticles, because the low temperature inhibits their diffusion to form larger precipitates. Recently done TEM observations on reconstructed specimens (Mathis 2014) have confirmed that hypothesis.

Gold and/or silver nanoparticles are known to provoke an optical absorption in a spectral range which will make the red colour of the cuprite disappear to leave a black result. That interpretation will be soon complemented by further investigation.

4. Metal gilding, a millenary technique

Gold foil and leaf have been used by most human civilisations since very early times to decorate all kinds of artwork materials: metal, stone, ceramic, wood, cartonnage of the Egyptian sarcophagi, glass. Most of the progresses done throughout centuries by the artisans are linked to two parameters: one is the evolution of the thickness of the gold film, starting from simple hammered foils with a thickness of several micrometres and progressively improved until obtaining very thin leaves of some tenth of micrometre. The second one is the continuous research on good adhesive material suitable for the various substrates to be gilded, as it is known that, thanks to its high natural surface energy, pure gold is one of the most difficult materials to apply on low surface energy substrates. Another way to insure a long-time conservation of a gilding film without the help of an adhesive “third material” is to use

thermal treatment, mercury amalgamation or a combination of both to obtain a structural interface between the substrate and the gold film, so metal gilding technology was more or less complemented around the beginning of the Christian Era by mercury (amalgam) gilding, a technology which involves a completely different know-how than leaf gilding. Both procedures were simultaneously used on metal objects until the middle of nineteenth century, when electrolytic deposition and electrotyping appeared. Simultaneously was developed in some geographic areas the surface depletion process to obtain gilded objects from copper-gold or silver-gold alloys.

That overview must be completed with the widespread procedure of using gold powder and a binder. The documentation given below is issued from a recent publication by the authors of a didactic opus (Darque-Ceretti and Aucouturier 2012), and references contained in it, devoted to the technical history of the various gilding procedures, based on the study by modern investigation techniques of a number of gilded museum objects.

4.1 Gold foil and leaf, the first gilding process

Gold thinning for being applied for decoration to art, funeral or cultic objects appeared as soon as more than 6000 years ago. It is well known that Egyptian gilders were already able to obtain gold foils by hammering (fig. 8) but also to transform these foils into gold leaves of less than 1 μm thickness as soon as the third millenary B.C. for instance to decorate sarcophagi.

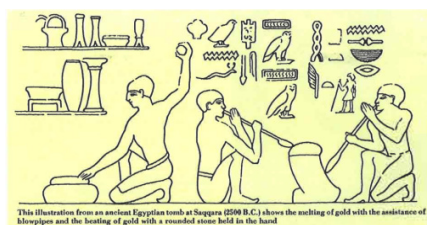


Fig. 8: Illustration from an Egyptian tomb in Saqqara. Ca 2500 B.C.

The figure 9 gives some examples of objects where gold leaves have been applied on various substrates: metal, wood, ivory, etc. The thickness of the gold leaves measured by the present authors was obtained by non-invasive RBS with the proton beam of the AGLAE particle accelerator.



Fig. 9: Some examples of leaf gilding on ancient objects. The leaf thickness is indicated when measured in authors' laboratory or (?) when approximated from the literature: (a) Syria, VIIIth cent. B.C., on ivory; (b) Meroe empire, ca 300 B.C., 7 μm , on bronze; (c) Egypt ca 200 B.C., 6 μm ?, on cartonage; (d) Arles, France, 1st cent. B.C., 1.5-2.5 μm , on bronze; (e) Lillebonne, France, ca 1.5 μm , on bronze; (f) Rio de Janeiro, Brazil, 0.2 μm ?, on wood; (g) Paris, France, 0.3 μm ?, on lead.

Leaf gilding is a complex operation with two main difficulties: (i) the mechanical know-how to obtain very thin gold leaves (down to 0.1 μm in modern time); (ii) the choice of an appropriate adhesive substance to obtain a durable adhesion on the substrate.

The first point implies a very sophisticated elaboration process. It has been indeed shown, and recently modelled and quantified (Felder 2010), that it is not possible by simple cold-rolling (or in ancient time hammering) to obtain gold foils thinner than a few micrometres (around 10 μm by modern cold-rolling). So another process has been invented, beating, where the hand worker strikes with a special hammer many thousand times a stack put on a flat anvil. That stack is composed of up to 2000 elements with alternatively gold foils and thicker inserts made of paper or polymer. Modelling the mechanical behaviour of the stack (Felder 2010) shows that the elastic deformation of the polymer inserts is responsible for progressive thinning of the gold foils. It is important to know that beating has been clearly invented already by the ancient Egyptian artisans. This means that the gold leaves thickness cannot be used as a dating criterion of gilded objects.

Solving the second problem gave rise to an important number of empirical recipes, proposed through the ages. It is impossible to give here an even simplified list of those recipes, which can be found in the literature (Darque-Ceretti and Aucouturier 2012, Bonaduce 2005). In summary, one often prepares the substrate surface by application of smooth and even layer of a powdered mix containing a binder and a charge finely grounded; on that layer an adhesive mixture is applied. The adhesives may be roughly classified in: i) proteinic glues as rabbit skin glue or fish glue, ii) glucidic compounds as honey, polysaccharides, starch, etc., iii) lipid compounds as linseed oil or other oils, sometimes containing siccative additives as lead compounds.

4.2 Mercury gilding, diffusion gilding

It seems that the process of mercury gilding appeared in China, and perhaps in Greece, around the IIIrd century B.C. The development of the technique in the Greco-Roman world was effective during the 1st century B.C. There is some confusion about the definition of the process, due to difficulties of interpretation of its mention in Pliny the Elder's encyclopaedia (Pliny the Elder, translation 1983). Indeed Pliny mentions a process based on the use of mercury as an adhesive to apply gold leaves on metals, and the process is usually referred in modern publications as cold mercury gilding, different from the fire gilding or amalgam gilding process. In that latter process gold fragments are first dissolved into liquid mercury at a moderate temperature to obtain an amalgam, and that amalgam is applied on the metal object which is then heated to a temperature higher than the mercury boiling point (356.5°C) to eliminate it. As underlined by some authors (Darque-Ceretti and Aucouturier 2012, Vittori 1979), the so-called cold gilding cannot be effective without a final heat treatment, which Pliny probably omits to mention. Figure 10 gives some examples of mercury (amalgam) gildings.



Fig. 10: Fire-gilded art objects: (a) the Hildesheim cathedral (Germany) Hezilo Leuchter, XIth cent., gilded copper, 2-5 μm ; (b) a panel of the Lorenzo Ghiberti's Door of Paradise in Firenze, 1452 CE, a few μm ?; (c) Firedogs executed by François Thomas-Germain, sculptor of King Louis the XVth (XVIIIth cent.), cast brass, Louvre museum, thickness 0.1 μm + important diffusion (10 μm).

Fire gilding, was used for gilding metal objects (silver, bronze and copper alloys, sometimes iron). It was practised simultaneously with less expensive leaf gilding, for the entire period between the beginnings of Christian Era to the middle of the XIXth century, when it was replaced, both for safety and cost reason, by electrolytic or electroless gilding.

It is clear that in mercury gilding, the interface between the gold surface film and the substrate is not two-dimensional. The adhesion is ensured thanks to some interdiffusion between the two components, the surface film and the underlying substrate. In fact, from the interface viewpoint, the problem is the same as in the so called diffusion gilding, practiced (quite rarely) in Middle Age, especially on silver, but also in the process called gilding à

l'haché, where the substrate is prepared by notching it to increase the contact surface with the leaf; then the leaf is carefully hammered on the surface. In those processes, adhesion is obtained through temperature increase or mechanical straining. To better understand those processes, it is useful to know the gold-substrate interdiffusion coefficients (Darque-Ceretti and Aucouturier 2012). For instance, the value of gold-silver interdiffusion coefficient is such that the diffusion distance of gold into a silver substrate at 330°C, a firing temperature commonly practiced by the professional metalworkers to evaporate mercury, is roughly of the order of 1 µm.

Another interesting point concerning mercury gilding is that interdiffusion induces an alloying of the gold film itself by mercury. Indeed, mercury is soluble in the solid state into gold. At 300-400°C, i.e. above the ebullition temperature of mercury, the gold layer may contain more than 10wt% of mercury in solid solution; which may be eliminated only by slow solid state diffusion.

4.3 Depletion gilding

A way to obtain a gold-looking surface at a lower cost was discovered at a neighbouring period in Central and South America, perhaps more confidentially in the Roman Empire around the first century CE. It is called depletion gilding or *miseencouleur* and the Latin America process is referenced as Tumbaga and Guamin. A gold-copper or gold-silver alloy is oxidised to eliminate the alloying element on a limited depth and the oxidation product is eliminated to leave a gold-enriched layer at the surface. The process is renewed several times to obtain a nearly pure gold coloured surface. The object is subsequently burnished to obtain a shining surface as the chemical etching has left a porous surface.

4.4 Electrochemical gilding

Nearly immediately after the invention of the Volta and Daniell electric cells, on the middle of the XIXth century, the use of electrical power for electrolytic deposition of gold on metals was proposed. Indeed that process was a long expected alternative to replace the health-hazardous mercury gilding, which was then prohibited, except for restoration.

In fact, metal gilding through an electrochemical process *strictosensu* was discovered much earlier. The ancient Latin American civilisations (as the Mochica kingdom in Peru during the seven first centuries CE) were already using the fact that gold is the noblest metal from the electrochemical potential viewpoint to provoke its deposition from liquid gold solution on a less noble metal as copper or silver. That process is used nowadays in electronic industry under the name of electroless gilding.

Concerning electrolysis gilding, using an electrical power source, it developed with a great success as soon as powerful DC electrical cells were available (Fig. 11), and even more when the other power generators as dynamos and hydroelectric generators became available from the end of the XIXth century. The Hildesheim Hezilolustre shown in figure 10a, although originally fire-gilded in the XIth century, has been repaired at the beginning of the XXth century with electrolysis-gilded pieces. The main drawback of the electrolysis process is the high toxicity of the gold solutions, often constituted of cyanide compounds. Modern processes promote new solutions, as sulphite ($\text{Na}_3\text{Au}(\text{SO}_3)_2$) or thiosulfate ($\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$).

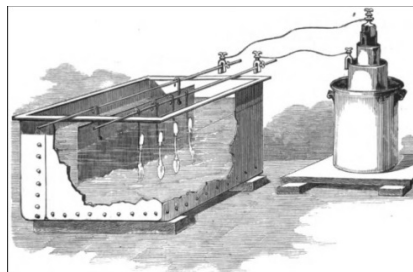


Fig. 11: Gold deposition tank and electrochemical cell power supply used in the Christofle Company, Paris, during the 1800's.

4.5 Other gilding processes

Another way to apply a gilt decoration is to use a gold powder dispersed in a binder, through a technique approaching colour painting. The oldest way, still used, to obtain a fine gold powder is to grind gold foils or gold leaves. A recent study on the characterisation of enamelled and gilded Syrian glass artefacts produced at the XIIIth-XIVth centuries (Gueit et al. 2010) showed that the leaf ground to prepare the gold powder was about 200 nm thick. As the process implied a final firing to ensure the adhesion of the powder to the glass substrate, the binder used for the application, probably organic, has disappeared and could not be identified. In the modern period, the use of gold decoration “painting” allows to multiply the kind of substrates (fabric wires, silk, leather, etc.) and simplifies the use of industrial serial production.

Liquid gold was developed after the 1920's and applied on table ware items for instance but also for industrial use. It uses a mixture containing gold organometallic compounds (e.g. sulforesinates, mercaptides, carboxylates, etc.) mixed with a resin and a number of additives. The paste is displayed on the object, e.g by screen-printing, and the item is fired to decompose the mixture and lead to precipitation of a gold thin film, whose thickness does not exceed 0.2 to 0.5 μm .

Physical deposition is done either by cathodic sputtering or evaporation under vacuum, largely used in the electronic industry. That process allows obtaining very thin and well controlled homogeneous films, down to a few atomic layers.

5. Fresco, a unique and very perennial wall painting technique

The fresco painting technique has been widely used throughout history, in particular at the Roman period, and is known to be the most durable form of mural painting. The traditional technique consists in applying “a fresco” water-dispersed pigments on a fresh lime plaster (the intonaco), which later hardens through carbonation mechanisms, i.e. the transformation of lime into calcium carbonate by reaction with carbon dioxide from the atmosphere (Delahousse 2009, Horgnies et al. 2014).

Following the invention of the Portland cement and the development of the concrete industry during the XXth century, some mural artists experienced a similar painting technique on cement plaster. The attempt was considered as impossible by most of the painters because the setting of cement is significantly faster than that of lime and does not involve carbonation. A couple of muralists tried nevertheless the technique with success. Indeed, H. Marret produced several frescoes painted either using the traditional lime or using a cement plaster.

Figures 12 shows some ancient and one modern frescoes on lime; Figure 13 shows a modern frescoes on cement.

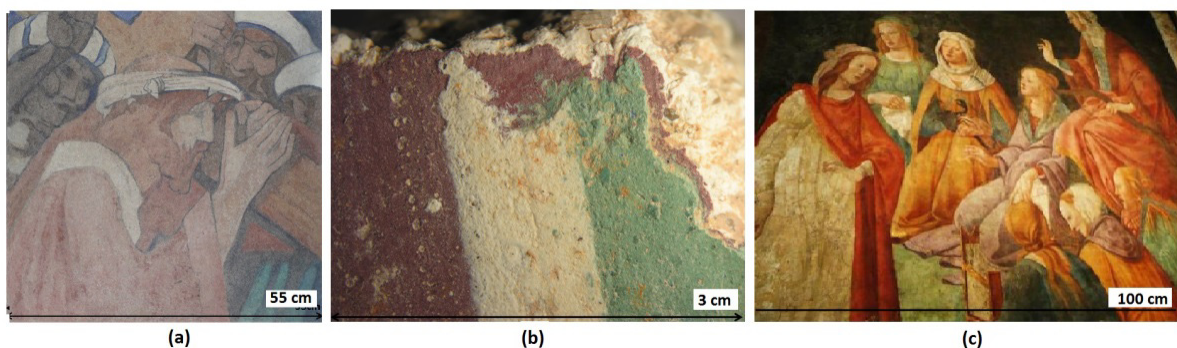


Fig. 12: Frescoes on lime. (a): detail of a panel belonging to the Stations of the Cross in the Sainte Croix church of Fourqueux (France) painted by H. Marret (1922); (b): fragment of a roman fresco from the Lero acropolis, Sainte Marguerite island, Mediterranean Sea (France) (1st century CE); (c) detail of one of the Botticelli frescoes (1463-1485), Louvre museum.



Fig. 13: St Hippolyte fresco on cement by H. Marret (1936). Saint Hippolyte church, Paris.

A special attention was given to the two artworks by H. Marret as they are an ideal comparison of a same painter using both fresco techniques on lime and on cement plaster, and this is why a large number of samples were taken, in order to be representative of the various parts of the decoration.

The aims of the study were (i) to understand the reason of the exceptional durability of the fresco paintings; (ii) to compare the techniques on lime and on cement and try to predict the durability of cement frescoes.

The experimental methodology was as follows:

- In situ (on the place of the artworks themselves), the frescoes were first examined and colorimetry measurements were done using the CIE $L^*a^*b^*$ colour representation (Gueit 2012). The $L^*a^*b^*$ space is useful to measure colour difference as the Euclidian distance between two points. In addition, the colour of a point between two others is a linear combination of the colours of those two other points weighed by the inverse distances between the intermediate point and them.

- Sampled micro-fragments of millimeter size (42 for the Saint-Hippolyte fresco, 24 for the Fourqueux fresco, several for the Lero fragment and the Botticelli frescoes) were taken to the laboratory to be submitted to X-ray diffraction (micro-XRD). They were also imbedded in epoxy resin and examined by optical (OM) and scanning electron (SEM) microscopies. Microanalysis was performed by SEM-EDS to identify the plasters compounds and the pigments.

5.1 Physico-chemical analyses

The Fourqueux lime-based intonaco is composed of portlandite $\text{Ca}(\text{OH})_2$ and calcite CaCO_3 plus quartz (from sand) as filler with a quite large grain size (0-5 mm). Its surface is rough with a high open porosity. The Saint-Hippolyte cement plaster is characteristic of a Portland cement mortar with portlandite $\text{Ca}(\text{OH})_2$, calcium silicate hydrates (C-S-H) and remaining clinker (anhydrous calcium silicates), plus ashes and quartz as fillers and coal as impurities. The grain size of the filler is also large (0-5 mm) and the surface is rough with a high open porosity. Combination of SEM observation and XRD shows that the cement plaster surface is covered by a film of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ of less than 20 μm thickness, which contains all the pigments.

In comparison with the Marret frescoes, the lime-based Lero frescoes surface does not show any rough aspect. The fillers are not clearly visible. For traditional Roman frescoes, the surface is dense and shiny. It has visibly been burnished by the painter before the complete setting. The frescoes from Botticelli are smooth (without apparent fillers) but do not seem as dense as the Lero frescoes.

The pigments are all mineral pigments. The ones used by H. Marret for the cement-based Saint Hippolyte fresco are only three: hematite Fe_2O_3 , goethite $\text{FeO}(\text{OH})$ and manganese oxide MnO_2 . This is in agreement with the indications of the painter who recommends using a limited range of pigments on a cement intonaco, probably because of possible chemical degradation. In the lime-based Fourqueux fresco, more than hematite and goethite, the SEM-EDS and XRD analyses show the presence of lazurite ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}$), chromium oxide (Cr_2O_3) and titanium oxide (TiO_2).

It is also interesting to compare the different thicknesses and microstructures of the pigmented layers. Figure 14a shows that the pigmented layer (pictorial layer) is clearly separated from the uncoloured intonaco in lime-based

frescoes, but may have different microstructures depending on the artist's work. In figure 14b, the thicknesses of the pigmented layers are compared. Thickness is very scattered even on the same artwork, but the cement-based fresco has the thinnest pictorial. This is easy to understand knowing that the cement setting is much faster than that of lime. As mentioned above, the pigments are contained in a surface layer of gypsum (CaSO_4 , $2 \text{H}_2\text{O}$). It is probable that the artist used a water solution of gypsum as a binder to color the fresco.

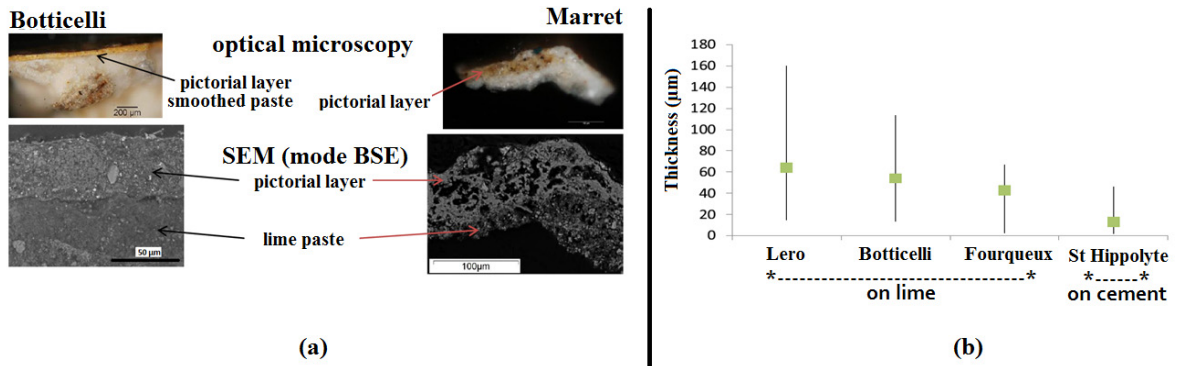


Fig. 14: (a) Optical microscopy and SEM (BSE mode) of cross sections of the lime-based frescoes by Botticelli and by H. Marret (Fourqueux panel); (b) summary of the thicknesses measured on the frescoes studied in the present work.

From those results, one understands why the frescoes are so resistant to environment aggression: (i) the pigment particles are imbedded into the first μm of the surface paste, apart from environmental influence; (ii) those pigments are mineral, i.e. neutral as respect to a possible chemical interaction with their binder (lime or cement).

5.2 Colorimetry

Colorimetric measurements done on frescoes produced by H. Marret are displayed in figure 15a as lightness (L^*) versus hue ($h = \arctan(b^*/a^*)$). The Fourqueux fresco painted on a white lime intonaco is clearer than the Saint-Hippolyte fresco. The painter palette of the Fourqueux artwork is richer than the one of Saint Hippolyte fresco where it is limited to the red and yellow hues. Despite using saturated blues and greens, the Fourqueux fresco is also made with a yellow dominance of the same chromatic range than the Saint Hippolyte fresco. Except the lightness difference due to the background difference, the data in the yellow-red range are very similar for both frescoes. H. Marret used probably the same pigments and processed them similarly in both cases.

In figure 15b are gathered in a $L^*a^*b^*$ representation all colorimetric points on the Saint Hippolyte fresco (cement plaster). The fresco is only constituted with four basic colours: black, yellow, red and cement colour, whose points are labelled as B (black or white, the (0,0) point by definition), Y (yellow), R (red) and C (the hydrated cement). Any other point can be described as a barycentre of three or four of those points and this confirms that the artist used only three pigments and variable mixtures of them. They are identified as two ochres, red hematite Fe_2O_3 and yellow goethite $\text{FeO}(\text{OH})$, and manganese-black MnO_2 .

Figure 16 shows the distribution of the colorimetric coordinates for the lime-based Fourqueux fresco. The artist used here a larger variety of hues than for Saint Hippolyte. Reds (hematite) are sometimes mixed with white (titanium oxide) to lighten them and sometimes with yellow (goethite) to obtain an orange hue. Greens (chromium oxide) are often added with blue (lazurite). The blue pigment can be used pure, mixed with red to give violet or applied on a pink background, respectively. The smaller surface of the Fourqueux panels and the fact that lime setting leaves more time to the painter than cement setting are probably responsible for that richer chromatic quality of the Fourqueux fresco.

It is difficult to tell if the frescoes by H. Marret, produced since only about one century, are going to exhibit durability as good as the Roman frescoes. However, they are still now in an excellent conservation state, even in the case of the cement-based fresco (Saint-Hippolyte) which is exposed to outdoor environment. One may think that, considering the results of the physico-chemical and colorimetric studies related here, their life is going to be long from now.

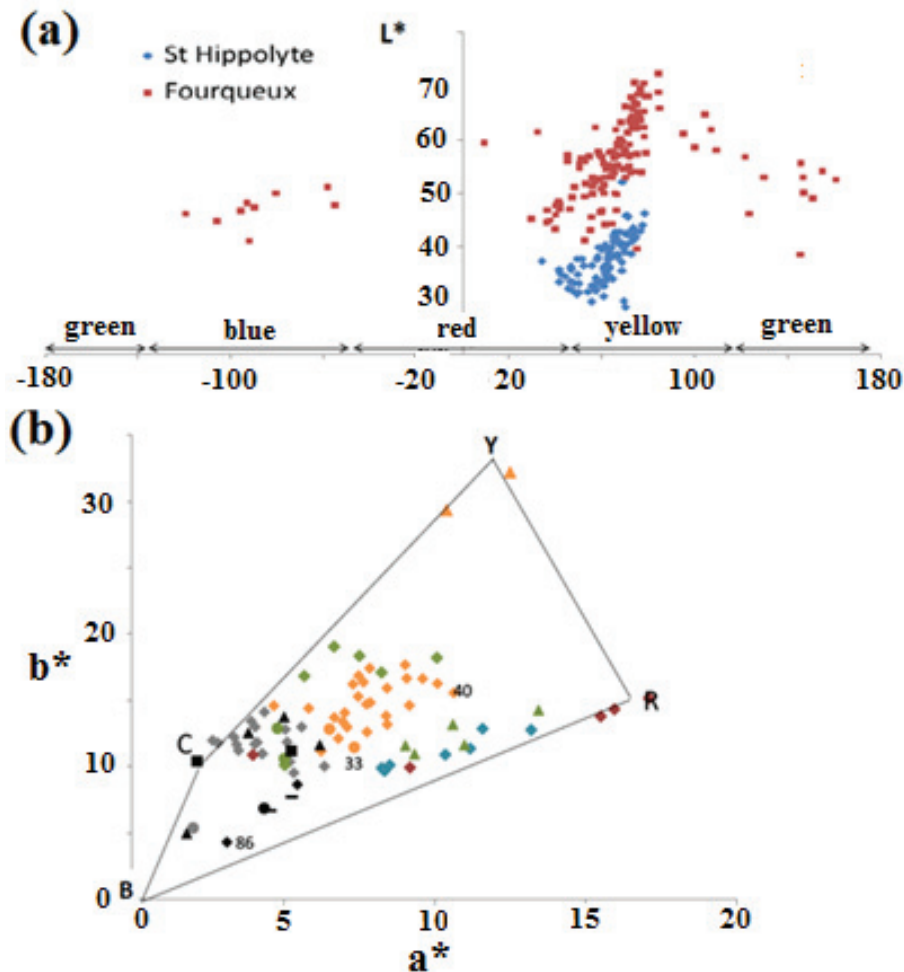


Figure 15: Colorimetric measurements on H. Marret's frescoes. (a) Positions of all measurements in the (lightness L^* versus hue $h = \arctan(b^*/a^*)$) plane; (b) position of the measured points on the Saint Hippolyte cement-based fresco in the (b^* versus a^*) plane.

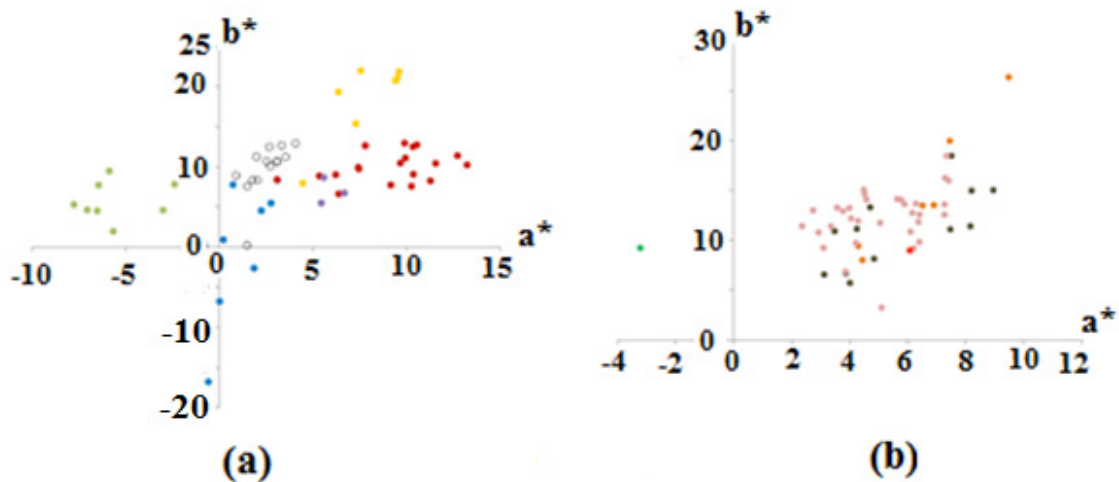


Figure 16: All colorimetric measurements on the H. Marret's lime-based Fourqueux fresco in the (b^* versus a^*) plane. (a) Character's clothes; (b) other items.

6. Conclusions

That series of examples of laboratory investigations on cultural heritage unique objects has shown, we hope, that it is possible to conduct very complete and very informative research programs on various domains of technical history, whatever the different materials involved in the fabrication of the artefacts. The recently brought availability of modern research instruments to the laboratories specialised in cultural heritage materials has drastically improved the scientific impact of the programs developed in those laboratories. It is important however to underline the necessity to keep always a multidisciplinary approach and involve in all the programs the collaboration between material scientists, historians, art historians, historians of techniques, archaeologists, conservators and museum curators.

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